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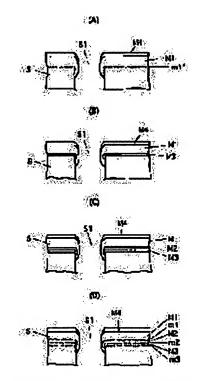
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# (54) COATING MATERIAL FOR MEDICAL USE

# (57)Abstract:

PROBLEM TO BE SOLVED: To suppress proliferation of bactera at a wound part for a long time and to prevent adhesion of coating to the wound part by coating the side to be abutted with the skin in an air permeable porous substrate with metallic coating having antibacterial activity and forming diamond-like carbon (DLC) adhesion preventing coating on the outside in a state in which the antibacterial metallic coating is partially exposed.

SOLUTION: On the side of the face to be contacted with the skin in a non- woven fabric coating substrate S of a high polymer material, antibacterial coating M1 composed of at least one kind among Ag, Au, Pt, Cu, Sn and Ir is formed by an ion vapor deposition thin coating



forming method, and furthermore, on the outside, DLC coating M4 is formed by a plasma CVD method. Their coating thickness is regulated to 0.5 to  $5\mu m$ , and, between the antibacterial coating M1 and the substrate S, a mixed layer m1' of both is allowed to exist to increase their adhesion. In this coating material for medical use, since the antibacterial coating M1 covers slightly to the inside of an air hole S1 of the substrate S, and on the other hand, the DLC coating 4 on the outside is not formed to the inside of the hole S1, the antibacterial coating M1 is partially exposed, and its activity can be shown (fig. A).

# **LEGAL STATUS**

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#### **CLAIMS**

## [Claim(s)]

[Claim 1] The medical-application cladding material characterized by forming the antibacterial film which is from the metal which has antimicrobial activity on the field side where reliance is divided into the skin of a medical-application cladding material base, and forming the diamond-like carbon (DLC) film in the condition that this antibacterial film is partially exposed to the outside of this antibacterial film.

[Claim 2] The medical-application cladding material according to claim 1 formed by the ion vacuum evaporationo thin film forming method said antibacterial film uses vacuum evaporationo and ion irradiation together.

[Claim 3] The medical-application cladding material according to claim 1 or 2 with which said antibacterial film consists of at least one sort of matter among silver (Ag), gold (Au), platinum (Pt), copper (Cu), zinc (Zn), tin (Sn), and iridium (Ir).

[Claim 4] The medical-application cladding material according to claim 1, 2, or 3 said whose base is a permeability porosity base and whose thickness of said antibacterial film is 0.5 micrometers or more 5 micrometers or less.

[Claim 5] The medical-application cladding material according to claim 4 whose thickness of said DLC film is 0.05 micrometers or more 0.5 micrometers or less.

[Claim 6] A medical-application cladding material given in either of claims 1-5 in which said DLC film is formed by the plasma-CVD method.

[Claim 7] A medical-application cladding material given in either of claims 1-6 which are what the base of said medical-application cladding material becomes from polymeric materials.

[Claim 8] The adhesion layer which consists of at least one sort of matter chosen as the field side where reliance is divided into the skin of a medical-application cladding material base from titanium (Ti), chromium (Cr), and silicon (Si) is formed. On the outside of this adhesion layer, silver (Ag), gold (Au), platinum (Pt), copper (Cu), The medical-application cladding material characterized by having formed the antibacterial film which consists of at least one sort of matter chosen from zinc (Zn), tin (Sn), and iridium (Ir), and forming the diamond-like carbon (DLC) film in the condition that this antibacterial film is partially exposed to the outside of this adhesion layer.

[Claim 9] The medical-application cladding material according to claim 8 formed by the ion vacuum evaporation thin film forming method at least one side uses vacuum evaporation and ion irradiation together among said adhesion layer and said antibacterial film.

[Claim 10] The medical-application cladding material according to claim 8 or 9 said whose base is a permeability porosity base and whose thickness of said antibacterial film is 0.5 micrometers or more 5 micrometers or less.

[Claim 11] The medical-application cladding material according to claim 10 whose thickness of said DLC film is 0.05 micrometers or more 0.5 micrometers or less.

[Claim 12] A medical-application cladding material given in either of claims 8-11 in which said DLC film is formed by the plasma-CVD method.

[Claim 13] A medical-application cladding material given in either of claims 8-12 which are what the base of said medical-application cladding material becomes from polymeric materials.

[Claim 14] The adhesion layer which consists of at least one sort of matter chosen as the field side where reliance is divided into the skin of a medical-application cladding material base from titanium (Ti), chromium (Cr), and silicon (Si) is formed. The barrier layer which consists of gold (Au), platinum (Pt) or gold, and platinum is formed in the outside of this adhesion layer. On the outside of this barrier layer, silver (Ag), platinum (Pt), copper (Cu), zinc (Zn), The medical-application cladding material characterized by having formed the antibacterial film which consists of at least one sort of matter chosen from tin (Sn) and iridium (Ir), and forming the diamond-like carbon (DLC) film in the condition that this antibacterial film is partially exposed to the outside of this antibacterial film.

[Claim 15] The medical-application cladding material according to claim 14 formed by the ion vacuum evaporation thin film forming method the film of [1 / at least] said adhesion layer, said barrier layer, and said antibacterial film (layer) uses vacuum evaporation and ion irradiation together.

[Claim 16] The medical-application cladding material according to claim 14 or 15 said whose base is a permeability porosity base and whose thickness of said antibacterial film is 0.5 micrometers or more 5 micrometers or less.

[Claim 17] The medical-application cladding material according to claim 16 whose thickness of said DLC film is 0.05 micrometers or more 0.5 micrometers or less.

[Claim 18] A medical-application cladding material given in either of claims 14-17 in which said DLC film is formed by the plasma-CVD method.

[Claim 19] A medical-application cladding material given in either of claims 14-18 which are what the base of said medical-application cladding material becomes from polymeric materials.

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#### DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the medical-application cladding material for protecting skin deficit parts, such as a medical-application cladding material especially the wound section, and the burn section.

[0002]

[Description of the Prior Art] The wound section of the skin, the burn section, etc. are usually covered with the medical-application cladding material (dry dressing material) for recovering by the incrustation, where this part is maintained at dryness, the medical-application cladding material (wet dressing material) for recovering by maintaining this part at a moderate damp or wet condition, and promoting the migration of an epidermal cell, etc., in order to protect this part. Although a desiccation necrosis of a wound is controlled and wet dressing material has prompt recovery, an exudate tends to collect between this wet dressing material and a wound side, and this part serves as an environment which bacteria etc. tend to increase.

[0003] About these medical-application cladding materials, in order to control growth of the bacteria in a wound side, to give the matter which has antimicrobial activity is tried. As antimicrobial activity matter given to a medical-application cladding material, an inorganic compound is used abundantly from a viewpoint of stability. For example, according to JP,64-15054,A, what included the zeolite which supported antibacterial metals, such as silver, copper, and zinc, in the front face or the whole of the medical-application cladding material which consists of silicone rubber is indicated.

[0004] Moreover, according to JP,4-90764,A and JP,4-272764,A, a hydrophilic polymer is chemically

combined with one front face of the medical-application cladding material of the shape of film which consists of porosity polyolefine and a thermoplastic polyurethane elastomer, respectively, and the thing which made extent which does not thin-film-ize an antibacterial metal by vacuum evaporationo or ion beam exposure adhere to this polymer plane of union further is indicated, for example.

[0005] Moreover, in case a wound side is covered with a medical-application cladding material, applying the cream pharmaceuticals containing an antimicrobial agent to a wound side, and preventing infection is also performed.

[0006]

[Problem(s) to be Solved by the Invention] However, it is easy to produce adhesion with a wound side, and both the aforementioned dry dressing material and wet dressing material have the problem that it is accompanied by pain at the time of dressing material exchange. Moreover, the aforementioned antibacterial zeolite is not applied to the front face of a medical-application cladding material, or the property of a base material may deteriorate by spreading and distribution of an antibacterial zeolite, and, generally the medical-application cladding material included in the whole is seldom used.

[0007] Moreover, although the metal is given to extent which is not thin-film-ized in the medical-application cladding material to which vacuum evaporationo etc. carried out the aforementioned antibacterial metal in order to avoid exfoliation of the metal membrane by crookedness of a base

material, since sufficient adhesion with a base material is not acquired in addition but it is easy to produce exfoliation of a metal while in use, it is difficult to maintain sufficient antimicrobial activity over long duration. Moreover, by the approach of applying the cream pharmaceuticals containing an antimicrobial agent, these the greater part of cream pharmaceuticals will be absorbed by the medical-application cladding material, and it takes the time and effort which effectiveness is bad and applies. [0008] Then, this invention makes it a technical problem to offer the medical-application cladding material which adhesion with a wound side cannot produce easily. Moreover, this activity can be maintained and used for it over a long time, and this invention makes it a technical problem to offer further the medical-application cladding material which adhesion with a wound side cannot produce easily while it has sufficient antimicrobial activity which can control growth of the bacteria in the wound section of the skin etc.

[0009]

[Means for Solving the Problem] The diamond-like carbon (DLC) film is formed in the condition that the antibacterial film which is from the metal which has antimicrobial activity on the field side where reliance is divided into the skin of the base of a medical-application cladding material is covered, and this antibacterial film exposes the medical-application cladding material of this invention to the outside of this antibacterial film partially.

[0010] The DLC film of the outermost layer is effective in adhesion control with a wound side. Although Ag which has strong antimicrobial activity typically can be mentioned as a metal which has said antimicrobial activity, noble metals, such as Au, Pt, and Ir, Cu, Zn, Sn, etc. can be used. Said antibacterial film can consist of at least one sort of matter among these.

[0011] As an ingredient of the medical-application cladding material base of this invention, synthetic macromolecule ingredients, such as naturally-ocurring-polymers ingredients, such as cotton usually used as an ingredient of a medical-application cladding material, polyethylene, and polyethylene terephthalate, etc. can be illustrated, and it is not limited especially. Moreover, the mode can illustrate the shape of the shape of a nonwoven fabric, and a film, the mode which piled up \*\*\*\*\*\*. The bases (for example, a nonwoven fabric, a film, etc. of permeability porosity which consist of polymeric materials) of the permeability porosity which consists of polymeric materials, such as cotton, polyethylene, and polyethylene terephthalate, as a typical thing can be mentioned. [0012] It is desirable for a base to make thickness of said antibacterial film 0.5-micrometer or more 5micrometer or less extent in the case of the base (for example, a porosity film and a nonwoven fabric base [ from ]) of permeability porosity. On the relation which forms the DLC film in the outermost layer, when this has thickness smaller than 0.5 micrometers the place where it is desirable for the antibacterial film to turn to the interior of a hole (opening) of not only the front face of a medicalapplication cladding material base but a base, it is difficult for it for the antibacterial film to turn to the interior of a hole (opening) of a base, and it is because there is a possibility that sufficient antimicrobial activity may not be obtained. Moreover, it is because it will be easy to produce a crack on the film and will become easy to produce exfoliation along with this crack, if larger than 5 micrometers. Moreover, thickness is said within the limits and is suitably defined according to the membranous quality of the material, the quality of the material of a medical-application cladding material base, the pore (opening) area of this base, etc. For example, it is possible to make thickness small at extent which permeability will worsen if an opening aspect product decreases remarkably by film formation to the inner skin of each opening, or an edge when choked up comparatively densely [ when the opening aspect product of this base is small (i.e., a front face) ], and does not decrease an opening aspect product remarkably since it is not desirable practically. Also for this reason, 5 micrometers or less are desirable. [0013] As for the thickness of said DLC film, it is desirable to consider as 0.05-micrometer or more (for example, 0.1 micrometers or more) 0.5-micrometer or less extent. It is difficult for this to carry out film

example, 0.1 micrometers or more) 0.5-micrometer or less extent. It is difficult for this to carry out film formation to homogeneity, if thickness is smaller than 0.05 micrometers, and it is because there is a possibility that the adhesion prevention effectiveness with sufficient wound side may not be acquired, and is because there is a possibility that the aforementioned antibacterial film may be extensively covered by the DLC film, and the antimicrobial activity of the antibacterial film may not fully be

demonstrated when larger than 0.5 micrometers.

[0014] Since the DLC film is formed in the surface part which touches the skin according to the medical-application cladding material of this invention, it is hard to adhere to a wound side, and the pain at the time of medical-application cladding material exchange becomes few things. Moreover, although the antibacterial film which becomes from the metal which has at least one sort of antimicrobial activity inside this DLC film is formed and this film is covered by the DLC film, since it has exposed partially For example, when adopting the aforementioned permeability porosity base, it can leave \*\*\*\*\*\* which is not covered with the DLC film by forming this film to the interior of a hole (opening) of this base. Such an antibacterial film exposure part and the exudate from a wound side contact, the antibacterial metal in this film is eluted in an exudate as ion, and the antimicrobial activity which the antibacterial film has is fully demonstrated.

[0015] In the medical-application cladding material of this invention, it is possible to have the adhesion layer which consists of at least one sort of matter among Ti, Cr, and Si between said medical-application cladding material bases and said antibacterial film. For example, when the antibacterial film is Ag film, Ti adhesion layer can be adopted. Each of these adhesion layer ingredients has comparatively good adjustment with the both sides of the ingredient adopted as an ingredient of usual medical-application cladding materials, such as polymeric materials, and said antibacterial film ingredient, and the role which raises the adhesion of this base and the antibacterial film is carried out.

[0016] Furthermore, in the medical-application cladding material of this invention, it has the barrier layer which consists of Au, Pt, or these both between said adhesion layers and said antibacterial film, and it is possible that said antibacterial film consists of at least one sort of matter among Ag, Pt, Ir, Cu, Zn, and Sn. For example, the antibacterial film can adopt the barrier layer which consists of Pt when an adhesion layer is a Ti layer by Ag film. When it does not have a barrier layer, there is a possibility that oxygen may be spread through the antibacterial film, and this oxygen reaches the interface part of the antibacterial film and an adhesion layer in that case, and it becomes easy to produce exfoliation of the antibacterial film in this part. Moreover, although it is easy to diffuse an antibacterial film constituent into an adhesion layer and the antibacterial film becomes easy to exfoliate in that case when it does not have a barrier layer, a barrier layer can control diffusion of such oxygen or (reaching) an antibacterial film constituent, and can raise the adhesion of the antibacterial film.

[0017] When forming the direct antibacterial film on a base in the medical-application cladding material of this invention, without forming an aforementioned adhesion layer and an aforementioned barrier layer, this film formation When it has the antibacterial film and an adhesion layer and has the antibacterial film, a barrier layer, and an adhesion layer for film (layer) formation of either or both sides, it is possible to perform film (layer) formation of at least 1 by the ion vacuum evaporationo thin film forming method which uses vacuum evaporationo and ion irradiation together.

[0018] Thereby, in an operation of exposure ion, while an ion irradiation side is activated, these both mixolimnion is formed between the formed film (layer) and its lower layer, and the adhesion of this film (layer) improves. As exposure ion, nitrogen ion, a hydrogen ion, inactive gas ion (helium (helium) ion, neon (Ne) ion, argon (Ar) ion, krypton (Kr) ion, xenon (Xe) ion, etc.), etc. can be used.

[0019] Although the acceleration voltage at the time of ion irradiation changes with quality of the materials of an ion kind and an ion irradiation side etc., it is desirable to consider as V or more 1002-kV or less extent. This is because there is a possibility that the effectiveness of ion irradiation may become an ununiformity in an exposure side, and the field whose film adhesion is not enough may be generated if smaller than 100V, and is because possibility that degradation of a medical-application cladding material base will arise under the effect of the heat accompanying ion irradiation is large when larger than 2kV.

[0020] Moreover, in the medical-application cladding material of this invention, as a medical-application cladding material base, it is possible to use what cleaned the front face by ion irradiation before film (layer) formation, and film (layer) adhesion becomes what was further excellent in this case. Thus, the long duration use of the formation film (layer) can be carried out by adopting the ion vacuum evaporationo thin film forming method, becoming what cannot exfoliate easily from the conventional

film also by crookedness of a base, and maintaining antimicrobial activity, as for such a cladding material.

[0021] Moreover, in the medical-application cladding material of this invention, said DLC film can illustrate what was typically formed by the plasma-CVD method, although especially the formation approach is not limited. In addition, since the adhesion of said DLC film and film (layer) of the inside is also good, the medical-application cladding material of this invention is formed on the base as the whole film at adhesion fitness.

[0022]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing. Drawing 1 (A), (B), (C), and (D) are some expanded sectional views of the medical-application cladding material which is the operation gestalt of this invention, respectively. The antibacterial film M1 which becomes the side which faces the skin at the time of use of the medicalapplication cladding material base S of the shape of a nonwoven fabric which consists of polymeric materials from at least one sort of matter among Ag, Au, Pt, Cu, Zn, Sn, and Ir is formed, the DLC film M4 is formed in the outside, and the medical-application cladding material shown in drawing (A) has these both mixolimnion m1' between the film M1 and Base S. The antibacterial film M1 has covered this medical-application cladding material to the some inside of the air hole (opening) S1 of not only the surface part of the medical-application cladding material base S but a base. On the other hand, the DLC film M4 of the outside is formed in the surface part of the antibacterial film M1, and is seldom formed to the hole S1. Therefore, the antibacterial film M1 is exposed partially and, thereby, antimicrobial activity is fully demonstrated. Moreover, since the DLC film M4 is formed in the surface part which touches the skin, it is hard to produce adhesion with a wound side. Moreover, of existence of mixolimnion m1', since it is good and the adhesion of the antibacterial film M1 and the DLC film M4 is also good, the adhesion of the film M1 and Base S is formed with adhesion sufficient on Base S as the whole film. [0023] The adhesion layer M3 which becomes the side by which the medical-application cladding material shown in drawing (B) faces the skin at the time of use of Base S from at least one sort of matter among Ti, Cr, and Si is formed, the antibacterial film M1 which consists of at least one sort of matter among Ag, Au, Pt, Cu, Zn, Sn, and Ir is formed in the outside, and the DLC film M4 is further formed in the outside. The antibacterial film M1 has covered this medical-application cladding material to the some inside of the air hole (opening) S1 of not only the surface part of the medical-application cladding material base S but a base. On the other hand, the DLC film M4 of the outside is formed in the surface part of the antibacterial film M1, and is seldom formed to the hole S1. Therefore, the antibacterial film M1 is exposed partially and, thereby, antimicrobial activity is fully demonstrated. Moreover, since the DLC film M4 is formed in the surface part which touches the skin, it is hard to produce adhesion with a wound side. Moreover, to the both sides of Base S and the film M1, since adjustment is good and the adhesion of the antibacterial film M1 and the DLC film M4 also has it, the adhesion layer M3 is formed with adhesion sufficient on Base S as the whole film. [good]

[0024] The medical-application cladding material shown in drawing (C) to the side which faces the skin at the time of use of Base S Ti, The adhesion layer M3 which consists of at least one sort of matter among Cr and Si is formed. The barrier layer M2 which consists of Au, Pt, or Au and Pt is formed in the outside, the antibacterial film M1 which consists of at least one sort of matter among Ag, Pt, Cu, Zn, Sn, and Ir is formed in the outside, and the DLC film M4 is further formed in the outside. The antibacterial film M1 has covered this medical-application cladding material to the some inside of the air hole (opening) S1 of not only the surface part of the medical-application cladding material base S but a base. On the other hand, the DLC film M4 of the outside is formed in the surface part of the antibacterial film M1, and is seldom formed to the hole S1. Therefore, the antibacterial film M1 is exposed partially and, thereby, antimicrobial activity is fully demonstrated. Moreover, since the DLC film M4 is formed in the surface part which touches the skin, it is hard to produce adhesion with a wound side. moreover, some film M1 by oxygen being spread from the exterior through the film M1, and collecting on the interface part of the film M1 and a layer M3, or the constituent of the film M1 being spread into a layer M3 by existence of the barrier layer M2, -- exfoliation is controlled.

[0025] Moreover, in the medical-application cladding material of drawing (C), the antibacterial film M1, the barrier layer M2, and the adhesion layer M3 are formed by each by the ion vacuum evaporationo thin film forming method, and the medical-application cladding material shown in drawing (D) has mixolimnions m1, m2, and m3 between the lower layer, respectively. This medical-application cladding material has respectively the adhesion much more good by existence of mixolimnions m1, m2, and m3 between the adhesion layer M3 and the medical-application cladding material base S between the barrier layer M2 and the adhesion layer M3 between the antibacterial film M1 and the barrier layer M2. [0026] In addition, in the medical-application cladding material of drawing (C), that in which the mixolimnion was formed only for one layer or two-layer by either is also considered. Moreover, also in the medical-application cladding material of drawing (B), what formed the antibacterial film M1 or (reaching) the adhesion layer M3 by the ion vacuum evaporation thin film forming method can be considered. Moreover, drawing 2 is drawing showing the outline configuration of the membrane formation equipment which can be used for formation of the antibacterial film, a barrier layer, and an adhesion layer in manufacture of the medical-application cladding material concerning this invention, respectively. This equipment has a vacuum housing 1 and an evaporation source 3 and the ion source 4 are formed in the location which counters the holder 2 and holder 2 which support the formed membranes medical-application cladding material base S in a container 1. Moreover, in the holder 2 neighborhood, the thickness monitor 5 and the ion current measuring instrument 6 are arranged. Moreover, an exhauster 11 is attached to a container 1 and the inside of a container 1 can be made into a predetermined degree of vacuum.

[0027] Moreover, drawing 3 is membrane formation equipment by the plasma-CVD method which can be used for formation of the DLC film in manufacture of the medical-application cladding material concerning this invention. this equipment -- vacuum housing 1' -- having -- container 1' -- the gas nozzle 8 is installed in the location which counters inside at an electrode 7 and this. RF generator 72 is connected to an electrode 7, and container 1' is grounded. Moreover, the heater 71 for heating the goods S supported on it formed membranes to membrane formation temperature is attached to the electrode 7. container 1 from stoma of a large number prepared in field which plasma material gas feed zone 9 is connected to gas nozzle 8, and counters electrode 7' -- plasma material gas can be introduced now inside. moreover, exhauster 11' attaches to container 1' -- having -- container 1' -- inside can be made into a predetermined degree of vacuum.

[0028] Next, the concrete example which manufactured the medical-application cladding material concerning this invention shown in said <u>drawing 1</u> (D) is explained using the equipment of <u>drawing 2</u> and <u>drawing 3</u>. As a formed membranes medical-application cladding material base S, the nonwoven fabric which consists of polyethylene terephthalate was used. After cleaning a base S front face ultrasonically with an alcoholic system organic solvent in advance of film formation, it was made to dry for 30 minutes at 60 degrees C. Subsequently, the medical-application cladding material base S was carried in in the container 1 of the equipment of <u>drawing 2</u>, and as film formation was carried out at the side to which reliance is divided into the skin at the time of use, after making a holder 2 support this base S, the inside of a container 1 was made into the degree of vacuum of 1x10 to 6 or less Torrs by operation of an exhauster 11.

[0029] Subsequently, from the ion source 4, Ar ion was irradiated with the acceleration voltage of 300V at Base S, and the base S front face was activated and cleaned. Then, evaporated Ti using the evaporation source 3, continuing Ar ion irradiation, it was made to vapor-deposit on the medical-application cladding material base S supported by the holder 2, and Ti adhesion layer M3 of 0.1 micrometers of thickness was formed on Base S. These both mixolimnion m3 was formed in the interface part of Base S and the adhesion layer M3 in connection with this.

[0030] Subsequently, vacuum evaporationo of Pt and the exposure of Ar ion as well as said Ti adhesion layer M3 formation were performed, and Pt barrier layer M2 of 0.1 micrometers of thickness was formed on Ti adhesion layer M3. These both mixolimnion m2 was formed in the interface part of the adhesion layer M3 and Pt barrier layer M2 in connection with this. Subsequently, vacuum evaporationo of Ag and the exposure of Ar ion were performed like said Ti adhesion layer M3 formation and said Pt

barrier layer M dimorphism \*\*, and the Ag antibacterial film M1 of 0.4 micrometers of thickness was formed on Pt barrier layer M2. These both mixolimnion m1 was formed in the interface part of Pt barrier layer M2 and the Ag antibacterial film M1 in connection with this.

[0031] In addition, the degree of vacuum in a vacuum housing 1 was maintained at abbreviation 4x10-5Torr during membrane formation. Subsequently, the film covering base with which Ti adhesion layer M3, Pt barrier layer M2, and the Ag antibacterial film M1 were formed in the base S front face at this order container 1' of the equipment of drawing 3 -- it carried in inside, and the field in which said film was formed in this film covering base was turned to the direction of a gas nozzle 8, it installed on the electrode 7, and the inside of a container 1 was made into the degree of vacuum of 1x10 to 5 or less Torrs by operation of exhauster 11'.

[0032] subsequently, the stoma prepared in the gas nozzle 8 from the gas supply section 9 -- letting it pass -- container 1' -- methane (CH4) gas inside container 1' -- from a power source 72 the frequency of 13.56MHz to an electrode 7, while introducing until an inner degree of vacuum is set to 1x10-3Torr The high-frequency power of power 300W was supplied, this plasma-ized said introduced plasma material gas, and the DLC film M4 of 0.1 micrometers of thickness was formed in the outside of the Ag antibacterial film M1 of said film covering base under this plasma.

[0033] Thus, as shown in drawing 1 (D), the medical-application cladding material with which the adhesion layer M3, the barrier layer M2, the antibacterial film M3, and the DLC film M4 were formed at this order on the field which contacts the skin at the time of use of the medical-application cladding material base S was obtained. Next, film adhesion was evaluated, respectively about the medical-application cladding material obtained according to said this invention example, the medical-application cladding material (example 1 of a comparison) which used together Ag vacuum evaporationo and Ar ion irradiation, and formed Ag film on Base S, and the medical-application cladding material (example 2 of a comparison) which formed Ag film only by vacuum evaporationo on Base S. After evaluation of film adhesion having given the include angle of about 180 degrees and making it crooked 50 times, applying a steam to the film forming face of each medical-application cladding material, performing the tape friction test (it being used on the property of the configuration of a specimen article, without cutting) according to observing a membranous condition with the naked eye and X cut tape test (JIS K5400) estimated it. A result is shown in degree table 1.

	膜の状態	Xカットテープ試験
実施例	剥離なし	剥離なし
比較例1	剥離なし	剥離なし
比較例2	剥離あり	全面剥離

Thus, it turns out that film adhesion even with after [good / the medical-application cladding material by the example 1 of a comparison which formed Ag film by each medical-application cladding material and the ion vacuum evaporationo thin film forming method by this invention example which formed each film (layer) by the ion vacuum evaporationo thin film forming method ] 50 times crookedness is shown, and it can be equal to long duration use. It turns out that exfoliation has produced the medical-application cladding material by the example 2 of a comparison which does not use ion irradiation together and, on the other hand, does not have an adhesion layer and a barrier layer by being crooked 50 times, and it is hard to present practical use.

[0034] Next, the ease of removing of coagulation blood was evaluated, respectively about the medical-application cladding material and the unsettled medical-application cladding material base S which has not carried out film formation obtained by said this invention example and the example 1 of a comparison. About 0.1ml of Homo sapiens blood is dropped on the film of each film covering base, and it is 2 1cm. Extended and applied to the area range, where this spreading part is covered with a petri dish, put, and blood was made to solidify, the friction test was performed using adhesive tape about the clot-of-blood film, and the ease of removing of coagulation blood was investigated. A result is shown in

degree table 2. 表 2

凝固血液の剥がし易さ

実施例容易に剥離比較例 1一部残存未処理基体ほば全面残存

Thus, it is thought that the medical-application cladding material of this invention example can remove easily the blood solidified on the film, and can remove it from the exudate which adhered to this medical-application cladding material when it used for the wound side where blood etc. oozed out easily. On the other hand, with Ag film covering base of the example 1 of a comparison, it is thought that it is a little difficult to remove from an exudate, and it is thought with an unsettled base with it that it is very difficult to remove from an exudate. [0035]

[Effect of the Invention] According to this invention, the medical-application cladding material which adhesion with a wound side cannot produce easily can be offered. Moreover, according to this invention, while having sufficient antimicrobial activity which can control growth of the bacteria in the wound section of the skin etc., this activity can be maintained and used over a long time, and the medical-application cladding material which adhesion with a wound side cannot produce easily can be offered further.

[Translation done.]

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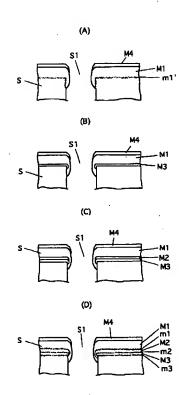
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## (54) 【発明の名称】 医療用被優材

## (57)【要約】

【課題】創傷面との癒着が生じ難い医療用被覆材を提供・ する。

【解決手段】医療用被覆材の基体Sの皮膚に当てがわれ る面側に抗菌活性を有する金属からなる抗菌性膜M1が 形成され、抗菌性膜M1の外側に、抗菌性膜M1が部分 的に露出する状態でダイヤモンド状炭素(DLC)膜M 4が形成されている医療用被覆材。



#### 【特許請求の範囲】

【請求項1】 医療用被覆材基体の皮膚に当てがわれる 面側に、抗菌活性を有する金属からなる抗菌性膜が形成 され、該抗菌性膜の外側に該抗菌性膜が部分的に露出す る状態でダイヤモンド状炭素(DLC)膜が形成されて いることを特徴とする医療用被覆材。

【請求項2】 前記抗菌性膜が蒸着とイオン照射を併用 するイオン蒸着薄膜形成法により形成されたものである 請求項1記載の医療用被覆材。

【請求項3】 前記抗菌性膜が銀(Ag)、金(Au)、白金(Pt)、銅(Cu)、亜鉛(Zn)、スズ(Sn)及びイリジウム(Ir)のうち少なくとも1種の物質からなっている請求項1又は2記載の医療用被覆材。

【請求項4】 前記基体が通気性多孔質基体であり、前記抗菌性膜の膜厚が0.5 μm以上5 μm以下である請求項1、2又は3記載の医療用被覆材。

【請求項5】 前記DLC膜の膜厚が0.05μm以上0.5μm以下である請求項4記載の医療用被覆材。

【請求項6】 前記DLC膜がプラズマCVD法により 形成されたものである請求項1から5のいずれかに記載 の医療用被覆材。

【請求項7】 前記医療用被覆材の基体が高分子材料からなるものである請求項1から6のいずれかに記載の医療用被覆材。

【請求項8】 医療用被覆材基体の皮膚に当てがわれる面側に、チタン(Ti)、クロム(Cr)及びシリコン(Si)から選ばれた少なくとも1種の物質からなる密着層が形成され、該密着層の外側に銀(Ag)、金(Au)、白金(Pt)、銅(Cu)、亜鉛(Zn)、スズ(Sn)及びイリジウム(Ir)から選ばれた少なくとも1種の物質からなる抗菌性膜が形成され、該密着層の外側に該抗菌性膜が部分的に露出する状態でダイヤモンド状炭素(DLC)膜が形成されたことを特徴とする医療用被覆材。

【請求項9】 前記密着層及び前記抗菌性膜のうち少なくとも一方が、蒸着とイオン照射を併用するイオン蒸着 薄膜形成法により形成されたものである請求項8記載の 医療用被覆材。

【請求項10】 前記基体が通気性多孔質基体であり、 前記抗菌性膜の膜厚が0.5μm以上5μm以下である 請求項8又は9記載の医療用被覆材。

【請求項11】 前記DLC膜の膜厚が0.05μm以上0.5μm以下である請求項10記載の医療用被覆材。

【請求項12】 前記DLC膜がプラズマCVD法により形成されたものである請求項8から11のいずれかに記載の医療用被覆材。

【請求項13】 前記医療用被覆材の基体が高分子材料からなるものである請求項8から12のいずれかに記載

の医療用被覆材。

【請求項14】 医療用被覆材基体の皮膚に当てがわれる面側に、チタン(Ti)、クロム(Cr)及びシリコン(Si)から選ばれた少なくとも1種の物質からなる密着層が形成され、該密着層の外側に金(Au)又は白金(Pt)又は金と白金からなるバリア層が形成され、該バリア層の外側に、銀(Ag)、白金(Pt)、銅(Cu)、亜鉛(Zn)、スズ(Sn)及びイリジウム(Ir)から選ばれた少なくとも1種の物質からなる抗菌性膜が形成され、該抗菌性膜の外側に該抗菌性膜が部分的に露出する状態でダイヤモンド状炭素(DLC)膜が形成されたことを特徴とする医療用被覆材。

【請求項15】 前記密着層、前記バリア層及び前記抗 菌性膜のうち少なくとも1の膜(層)が、蒸着とイオン 照射を併用するイオン蒸着薄膜形成法により形成された ものである請求項14記載の医療用被覆材。

【請求項16】 前記基体が通気性多孔質基体であり、 前記抗菌性膜の膜厚が0.5μm以上5μm以下である 請求項14又は15記載の医療用被覆材。

【請求項17】 前記DLC膜の膜厚が0.05μm以上0.5μm以下である請求項16記載の医療用被覆材。

【請求項18】 前記DLC膜がプラズマCVD法により形成されたものである請求項14から17のいずれかに記載の医療用被覆材。

【請求項19】 前記医療用被覆材の基体が高分子材料 からなるものである請求項14から18のいずれかに記 載の医療用被覆材。

#### 【発明の詳細な説明】

#### [0001]

【発明の属する技術分野】本発明は、医療用被覆材、特に創傷部、熱傷部等の皮膚欠損部位を保護するための医療用被覆材に関する。

#### [0002]

【従来の技術】皮膚の創傷部、熱傷部等は、通常、該部位を保護するために、該部位を乾燥状態に保った状態で 施皮形成により治癒を行うための医療用被覆材 (ドライドレッシング材) や、該部位を適度の湿潤状態に保ち表皮細胞の遊走を促進することにより治癒を行うための医療用被覆材 (ウェットドレッシング材) 等で覆われる。ウェットドレッシング材は、創傷の乾燥壊死が抑制されて治癒が速やかであるが、滲出液が該ウェットドレッシング材と創傷面との間に溜まり易く、該部分は細菌等が 増殖し易い環境となる。

【0003】これらの医療用被覆材については、創傷面での細菌の増殖を抑制するために、抗菌活性を有する物質を付与することが試みられている。医療用被覆材に付与する抗菌活性物質としては、安定性の観点から無機化合物が多用される。例えば、特開昭64-15054号公報によると、銀、銅、亜鉛等の抗菌性金属を担持した

ゼオライトを、シリコンゴムからなる医療用被覆材の表 面或いは全体に含ませたものが開示されている。

【0004】また、例えば特開平4-90764号公報及び特開平4-272764号公報によると、それぞれ多孔質ポリオレフィン及び熱可塑性ポリウレタンエラストマーからなる膜状の医療用被覆材の一方の表面に親水性ポリマーを化学的に結合させ、さらに該ポリマー結合面に抗菌性金属を蒸着又はイオンビーム照射により、薄膜化しない程度に付着させたものが開示されている。

【0005】また、医療用被覆材で創傷面を被覆する際、創傷面に抗菌剤を含有するクリーム剤を塗布して感染を予防することも行われている。

#### [0006]

【発明が解決しようとする課題】しかしながら、前記のドライドレッシング材、ウェットドレッシング材のいずれも、創傷面との癒着が生じ易く、ドレッシング材交換時に苦痛を伴うという問題がある。また、前記の、抗菌性ゼオライトを医療用被覆材の表面に塗布したり、全体に含ませたりした医療用被覆材は、抗菌性ゼオライトの塗布や分散により基材の特性が劣化する場合があり、一般的にはあまり使用されていない。

【00007】また、前記の抗菌性金属を蒸着等させた医療用被覆材では、基材の屈曲による金属膜の剥離を避けるため、薄膜化しない程度に金属を付与してはいるものの、なお基材との十分な密着性が得られず、使用中に金属の剥離が生じ易いため、長時間にわたり十分な抗菌活性を維持することが困難である。また、抗菌剤を含むクリーム剤を塗布する方法では、該クリーム剤の大部分が医療用被覆材に吸収されてしまい効率が悪く、また塗布する手間がかかる。

【0008】そこで本発明は、創傷面との癒着が生じ難い医療用被覆材を提供することを課題とする。また本発明は、皮膚の創傷部等での細菌の増殖を抑制できるだけの十分な抗菌活性を有するとともに、該活性を長時間にわたり維持して使用することができ、さらに、創傷面との癒着が生じ難い医療用被覆材を提供することを課題とする。

#### [0009]

【課題を解決するための手段】本発明の医療用被覆材は、医療用被覆材の基体の皮膚に当てがわれる面側に、抗菌活性を有する金属からなる抗菌性膜が被覆され、該抗菌性膜の外側に該抗菌性膜が部分的に露出する状態でダイヤモンド状炭素 (DLC) 膜が形成されたものである。

【0010】最外層のDLC膜は創傷面との癒着抑制に有効である。前記抗菌活性を有する金属としては、代表的には強い抗菌力を有するAgを挙げることができるが、この他Au、Pt、Ir等の貴金属やCu、Zn、Sn等も用いることができる。前記抗菌性膜はこれらのうち少なくとも1種の物質で構成することができる。

【0011】本発明の医療用被覆材基体の材料としては、医療用被覆材の材料として通常用いられている綿等の天然高分子材料、ポリエチレン、ポリエチレンテレフタレート等の合成高分子材料等を例示でき、特に限定されない。また、その態様は、不織布状、フィルム状、や織物を重ねた態様等を例示できる。代表的なものとして綿、ポリエチレン、ポリエチレンテレフタレート等の高分子材料からなる通気性多孔質の基体(例えば高分子材料からなる通気性多孔質の不織布やフィルム等)を挙げることができる。

【0012】基体が通気性多孔質の基体(例えば、多孔 質フィルムや不織布からな基体) の場合、前記抗菌性膜 の膜厚は0. 5 μ m以上5 μ m以下程度とすることが望 ましい。これは、最外層にDLC膜を形成する関係上、 医療用被覆材基体の表面のみならず基体の孔(開口部) 内部まで抗菌性膜がまわり込むことが望ましいところ、 膜厚が0.5μmより小さいと、基体の孔(開口部)内 部まで抗菌性膜がまわり込むことが難しく、十分な抗菌 活性が得られない恐れがあるからである。また、5μm より大きいと、膜にクラックが生じ易く、このクラック に沿って剥離が生じ易くなるからである。また、膜厚 は、前記範囲内で膜の材質、医療用被覆材基体の材質、 該基体の孔部(開口部)面積等に応じて適宜定める。例 えば、該基体の開口部面積が小さい場合、すなわち表面 が比較的密に詰まっている場合、各開口部の内周面や縁 への膜形成により開口部面積が著しく減小すると、通気 性が悪くなり実用上好ましくないため、開口部面積を著 しく減小しない程度に膜厚を小さくすることが考えられ る。このためにも5μm以下が望ましい。

【0013】前記DLC膜の膜厚は、 $0.05\mu$ m以上(例えば $0.1\mu$ m以上) $0.5\mu$ m以下程度とすることが望ましい。これは、膜厚が $0.05\mu$ mより小さいと、膜形成を均一に行うことが難しく、十分な創傷面との癒着防止効果が得られない恐れがあるからであり、 $0.5\mu$ mより大きいと、前記の抗菌性膜が全面的にDLC膜で覆われてしまって抗菌性膜の抗菌活性が十分に発揮されない恐れがあるからである。

【0014】本発明の医療用被覆材によると、皮膚と接する表面部分にDLC膜が形成されているため、創傷面と癒着し難く、医療用被覆材交換時の苦痛が少ないものとなる。また、該DLC膜の内側には少なくとも1種の抗菌活性を有する金属からなる抗菌性膜が形成され、該膜はDLC膜に被覆されているものの部分的に露出しているので、例えば前記の通気性多孔質基体を採用する場合、該膜を該基体の孔(開口)内部まで形成することでDLC膜に覆われないる部分を残しておくことができ、このような抗菌性膜露出部分と創傷面からの滲出液とが接触して該膜中の抗菌性金属がイオンとして滲出液中に溶出し、抗菌性膜の有する抗菌活性が十分に発揮される。

【0015】本発明の医療用被覆材において、前記医療用被覆材基体と前記抗菌性膜との間に、Ti、Cr及びSiのうち少なくとも1種の物質からなる密着層を有することが考えられる。例えば、抗菌性膜がAg膜の場合においてTi密着層を採用することができる。これらの密着層材料はいずれも、高分子材料等の通常医療用被覆材の材料として採用される材料及び前記抗菌性膜材料の双方との整合性が比較的良く、該基体と抗菌性膜との密着性を高める役割をする。

【0016】さらに、本発明の医療用被覆材において、前記密着層と前記抗菌性膜との間にAu又はPt又は該両者からなるバリア層を有し、前記抗菌性膜がAg、Pt、Ir、Cu、Zn、Snのうち少なくとも1種の物質からなることが考えられる。例えば、抗菌性膜がAg膜で密着層がTi層の場合において、Ptからなるバリア層を採用することができる。バリア層を有しない場合、抗菌性膜を通して酸素が拡散する恐れがあり、その場合該酸素が抗菌性膜と密着層との界面部分に達して該部分での抗菌性膜の剥離が生じ易くなる。また、バリア層を有しない場合、抗菌性膜構成物質が密着層内へ拡散し易く、その場合抗菌性膜が剥離し易くなるが、バリア層はこのような酸素又は(及び)抗菌性膜構成物質の拡散を抑制し、抗菌性膜の密着性を向上させることができる。

【0017】本発明の医療用被覆材において、前記の密 着層やバリア層を形成することなく基体上に直接抗菌性 膜を形成する場合は該膜形成を、抗菌性膜及び密着層を 有するときにはいずれか一方又は双方の膜(層)形成 を、抗菌性膜、バリア層及び密着層を有するときには少 なくとも1の膜(層)形成を、蒸着とイオン照射を併用 するイオン蒸着薄膜形成法により行うことが考えられ る。

【0018】これにより、照射イオンの作用で、イオン 照射面が活性化されるとともに、形成した膜(層)とその下層との間に該両者の混合層が形成されて、該膜

(層) の密着性が向上する。照射イオンとしては、窒素 イオン、水素イオン、不活性ガスイオン(ヘリウム(H e) イオン、ネオン (Ne) イオン、アルゴン (Ar) イオン、クリプトン (Kr) イオン、キセノン (Xe) イオン等) 等を用いることができる。

【0019】イオン照射時の加速電圧はイオン種、イオン照射面の材質等により異なるが、100V以上2kV以下程度とすることが望ましい。これは、100Vより小さいと、イオン照射の効果が照射面内で不均一になり、膜密着性が十分でない領域が生じる恐れがあるからであり、2kVより大きいと、イオン照射に伴う熱の影響で医療用被覆材基体の劣化が生じる可能性が大きいからである。

【0020】また、本発明の医療用被覆材において、医療用被覆材基体として、膜(層)形成前にイオン照射に

より表面をクリーニングしたものを用いることが考えられ、この場合、膜(層)密着性が一層優れたものとなる。このように、イオン蒸着薄膜形成法を採用することで、形成膜(層)が基体の屈曲によっても従来の膜より剥離し難いものとなり、このような被覆材は抗菌活性を維持したまま長時間使用できる。

【0021】また、本発明の医療用被覆材において、前 記DLC膜はその形成方法は特に限定されないが、代表 的にはプラズマCVD法により形成されたものを例示で きる。なお、本発明の医療用被覆材は、前記DLC膜と その内側の膜(層)との密着性も良いことから膜全体と して基体上に密着性良好に形成されている。

#### [0022]

【発明の実施の形態】以下、本発明の実施の形態を図面 を参照して説明する。図1(A)、(B)、(C)及び (D) はそれぞれ本発明の実施形態である医療用被覆材 の一部の拡大断面図である。図(A)に示す医療用被覆 材は高分子材料からなる不織布状の医療用被覆材基体S の、使用時に皮膚に面する側にAg、Au、Pt、C u、Zn、Sn及びIrのうち少なくとも1種の物質か らなる抗菌性膜M1が形成され、その外側にDLC膜M 4が形成され、膜M1と基体Sとの間に該両者の混合層 m1´を有するものである。この医療用被覆材は、抗菌 性膜M1が医療用被覆材基体Sの表面部分のみならず基 体の通気孔(開口)S1の若干内側までも覆っている。 一方、その外側のDLC膜M4は抗菌性膜M1の表面部 分に形成され、孔S1まではあまり形成されていない。 従って、抗菌性膜M1は部分的に露出しており、これに より抗菌活性は十分に発揮される。また、皮膚と接する 表面部分にはDLC膜M4が形成されているため創傷面 との癒着が生じ難い。また、混合層m 1 の存在により 膜M1と基体Sとの密着性は良好であり、抗菌性膜M1 とDLC膜M4との密着性も良好であることから、膜全 体として基体S上に密着性良く形成されている。

【0023】図(B)に示す医療用被覆材は、基体S の、使用時に皮膚に面する側にTi、Cr及びSiのう ち少なくとも1種の物質からなる密着層M3が形成さ れ、その外側にAg、Au、Pt、Cu、Zn、Sn及 びIrのうち少なくとも1種の物質からなる抗菌性膜M 1が形成され、さらにその外側にDLC膜M4が形成さ れたものである。この医療用被覆材は、抗菌性膜M1が 医療用被覆材基体Sの表面部分のみならず基体の通気孔 (開口) S1の若干内側までも覆っている。一方、その 外側のDLC膜M4は抗菌性膜M1の表面部分に形成さ れ、孔S1まではあまり形成されていない。従って、抗 菌性膜M1は部分的に露出しており、これにより抗菌活 性は十分に発揮される。また、皮膚と接する表面部分に はDLC膜M4が形成されているため創傷面との癒着が 生じ難い。また、密着層M3が基体Sと膜M1の双方に 対し整合性がよく、抗菌性膜M1とDLC膜M4との密

着性も良好であることから、膜全体として基体S上に密 着性良く形成されている。

【0024】図(C)に示す医療用被覆材は、基体S の、使用時に皮膚に面する側にTi、Cr及びSiのう ち少なくとも1種の物質からなる密着層M3が形成さ れ、その外側にAu、Pt又はAu及びPtからなるバ リア層M2が形成され、その外側にAg、Pt、Cu、 Zn、Sn及びIrのうち少なくとも1種の物質からな る抗菌性膜M1が形成され、さらにその外側にDLC膜 M4が形成されたものである。この医療用被覆材は、抗 菌性膜M1が医療用被覆材基体Sの表面部分のみならず 基体の通気孔(開口)S1の若干内側までも覆ってい る。一方、その外側のDLC膜M4は抗菌性膜M1の表 面部分に形成され、孔S1まではあまり形成されていな い。従って、抗菌性膜M1は部分的に露出しており、こ れにより抗菌活性は十分に発揮される。また、皮膚と接 する表面部分にはDLC膜M4が形成されているため創 傷面との癒着が生じ難い。また、バリア層M2の存在に より、膜M1を介して外部から酸素が拡散して膜M1と 層M3との界面部分に溜まったり、膜M1の構成成分が 層M3内へ拡散したりすることによる膜M1の一部剥離 が抑制されている。

【0025】また、図(D)に示す医療用被覆材は、図(C)の医療用被覆材において、抗菌性膜M1、バリア層M2、密着層M3がいずれもイオン蒸着薄膜形成法により形成されたものであり、それぞれその下層との間に混合層m1、m2、m3を有している。この医療用被覆材は、混合層m1、m2、m3の存在により、抗菌性膜M1とバリア層M2と密着層M3との間、ベリア層M2と密着層M3との間、密着層M3と医療用被覆材基体Sとの間の密着性がそれぞれ一層良好なものである。

【0026】なお、図(C)の医療用被覆材において、混合層がいずれかに1層又は2層のみ形成されたものも考えられる。また、図(B)の医療用被覆材においても、抗菌性膜M1又は(及び)密着層M3をイオン蒸着薄膜形成法により形成したものが考えられる。また、図2は本発明に係る医療用被覆材の製造において抗菌性膜、バリア層及び密着層の形成にそれぞれ用いることができる成膜装置の概略構成を示す図である。この装置は真空容器1を有し、容器1内には被成膜医療用被覆材基体Sを支持するホルダ2及びホルダ2に対向する位置に蒸発源3及びイオン源4が設けられている。また、ホルダ2付近には膜厚モニタ5及びイオン電流測定器6が配置されている。また、容器1には排気装置11が付設されて容器1内を所定の真空度にすることができる。

【0027】また、図3は本発明に係る医療用被覆材の 製造においてDLC膜の形成に用いることができるプラ ズマCVD法による成膜装置である。この装置は、真空 容器1 を有し、容器1 内には電極7及びこれに対向 する位置にガスノズル8が設置されている。電極7には 高周波電源72が接続され、容器1 ´ は接地されている。また、電極7にはその上に支持される被成膜物品Sを成膜温度に加熱するためのヒータ71が付設されている。ガスノズル8にはプラズマ原料ガス供給部9が接続されており、電極7に対向する面に設けられた多数の小孔から容器1 ´ 内にプラズマ原料ガスを導入できるようになっている。また、容器1 ´ には排気装置11 ´ が付設されて容器1 ´ 内を所定の真空度にすることができる。

【0028】次に、図2及び図3の装置を用いて、本発明に係る、前記図1 (D)に示す医療用被覆材を製造した具体的実施例について説明する。被成膜医療用被覆材基体Sとして、ポリエチレンテレフタレートからなる不織布を用いた。膜形成に先立ち、基体S表面を、アルコール系有機溶媒で超音波洗浄した後、60℃で30分間乾燥させた。次いで、図2の装置の容器1内に医療用被覆材基体Sを搬入し、該基体Sを使用時に皮膚に当てがわれる側に膜形成されるようにして、ホルダ2に支持させた後、排気装置11の運転にて容器1内を1×10<sup>-6</sup> Torr以下の真空度とした。

【0029】次いで、イオン源4からArイオンを300Vの加速電圧で基体Sに照射し、基体S表面を活性化及びクリーニングした。その後、Arイオン照射を継続しながら蒸発源3を用いてTiを蒸発させ、ホルダ2に支持された医療用被覆材基体S上に蒸着させて、基体S上に層厚0.1 $\mu$ mのTi密着層M3を形成した。これに伴い、基体Sと密着層M3との界面部分に該両者の混合層m3が形成された。

【0030】次いで、前記Ti密着層M3形成と同様にしてPtの蒸着とArイオンの照射を行い、Ti密着層M3上に層厚0.1μmのPtバリア層M2を形成した。これに伴い、密着層M3とPtバリア層M2との界面部分に該両者の混合層m2が形成された。次いで、前記Ti密着層M3形成及び前記Ptバリア層M2形成と同様にしてAgの蒸着とArイオンの照射を行い、Ptバリア層M2上に膜厚0.4μmのAg抗菌性膜M1を形成した。これに伴い、Ptバリア層M2とAg抗菌性膜M1との界面部分に該両者の混合層m1が形成された

【0031】なお、成膜中は真空容器1内の真空度を約4×10<sup>-5</sup>Torrに保った。次いで、基体S表面にTi密着層M3、Ptバリア層M2及びAg抗菌性膜M1がこの順に形成された膜被覆基体を、図3の装置の容器1<sup>-</sup>内に搬入し、該膜被覆基体を前記膜が形成された面をガスノズル8の方に向けて電極7上に設置し、排気装置11<sup>-</sup>の運転にて容器1内を1×10<sup>-5</sup>Torr以下の真空度とした。

【0032】次いで、ガス供給部9からガスノズル8に設けられた小孔を通して容器1 内にメタン( $CH_4$ )ガスを、容器1 内の真空度が $1 \times 10^{-3}$  T or r にな

るまで導入するとともに電極7に電源72から周波数1 3. 56MHz、電力300Wの高周波電力を供給し、 これにより前記導入したプラズマ原料ガスをプラズマ化 し、該プラズマの下で前記膜被覆基体のAg抗菌性膜M 1の外側に膜厚0. 1μmのDLC膜M4を形成した。 【0033】このようにして、図1 (D) に示すよう に、医療用被覆材基体Sの、使用時に皮膚と接触する面 上に密着層M3、バリア層M2、抗菌性膜M3及びDL C膜M4がこの順に形成された医療用被覆材を得た。次 に、前記本発明実施例により得られた医療用被覆材、基 体S上にAg蒸着とArイオン照射を併用してAg膜を 形成した医療用被覆材(比較例1)、及び基体S上に蒸 着のみによりAg膜を形成した医療用被覆材(比較例 2) について、それぞれ膜密着性を評価した。膜密着性 の評価は、各医療用被覆材の膜形成面に水蒸気を当てな がら、約180度の角度をつけて50回屈曲させた後、 膜の状態を肉眼で観察すること及びXカットテープ試験 (JIS K5400) に準じたテープ剥離試験(被検 物品の形状の特性上、カットせずに使用)を行うことで 評価した。結果を次表1に示す。

#### 表1

膜の状態 Xカットテープ試験

実施例 剥離なし

剥離なし

比較例1 剥離なし

剥離なし

このより終例をオン製業強度形成法に全面製作(層)を 形成した本発明実施例による各医療用被覆材及びイオン 蒸着薄膜形成法により Ag膜を形成した比較例1による 医療用被覆材は、50回屈曲後も良好な膜密着性を示 し、長時間使用に耐え得ることが分かる。一方、イオン 照射を併用せず、また密着層及びバリア層を有しない比 較例2による医療用被覆材は、50回屈曲することによ り、剥離が生じており、実用に供し難いことが分かる。 【0034】次に、前記本発明実施例、比較例1により 得られた医療用被覆材及び膜形成していない未処理の医 療用被覆材基体Sについて、それぞれ凝固血液の剥がし 易さを評価した。各膜被覆基体の膜上にヒト血液約0. 1mlを滴下して1cm2の面積範囲に広げて塗布し、 該塗布部分をシャーレで覆った状態で静置して血液を凝 固させ、凝血膜について粘着テープを用いて剥離試験を 行い、凝固血液の剥がし易さを調べた。結果を次表2に 示す。

表2

経固血液の剥がし易さ

実施例

容易に剥離

比較例1

一部残存

このように未必要制度施例の医療情報を存む、膜上で凝固した血液を容易に剥がすことができ、血液等が滲出し

た創傷面に用いた場合に該医療用被覆材と癒着した滲出液から容易に剥がすことができると考えられる。一方、比較例1のAg膜被覆基体では、滲出液から剥がすことがやや難しいと考えられ、未処理の基体では滲出液から剥がすことが非常に難しいと考えられる。

#### [0035]

【発明の効果】本発明によると、創傷面との癒着が生じ 難い医療用被覆材を提供することができる。また本発明 によると、皮膚の創傷部等での細菌の増殖を抑制できる だけの十分な抗菌活性を有するとともに、該活性を長時 間にわたり維持して使用することができ、さらに、創傷 面との癒着が生じ難い医療用被覆材を提供することがで きる

#### 【図面の簡単な説明】

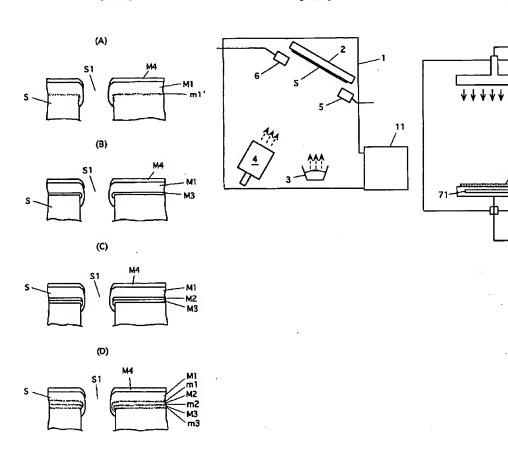
【図1】図(A)、(B)、(C)及び(D)は、それぞれ本発明の実施形態である医療用被覆材の一部の拡大断面図である。

【図2】本発明に係る医療用被覆材の製造において、密 着層、バリア層及び抗菌性膜の形成にそれぞれ用いるこ とができる成膜装置の概略構成を示す図である。

【図3】本発明に係る医療用被覆材の製造において、D LC膜の形成に用いることができる成膜装置の概略構成 を示す図である。

#### 【符号の説明】

- 1、1 真空容器
- 11、11 排気装置
- 2 被成膜物品支持ホルダ
- 3 蒸発源
- 4 イオン源
- 5 膜厚モニタ
- 6 イオン電流測定器
- 7 髙周波電極
- 71 ヒータ
- 72 高周波電源
- 8 ガスノズル
- 9 プラズマ原料ガス供給部
- S 医療用被覆材基体
- M1 抗菌性膜
- M2 バリア層
- M3 密着層
- M4 DLC膜
- m1、m1、m2、m3 混合層



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